

## **BLUE, BLACK AND PURPLE! THE SPECIAL COLOURS OF GOLD.**

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### **Introduction**

Gold is unique amongst the precious metals in having a colour – a warm, deep yellow colour. It is also unique in that conventional carat gold jewellery can be produced in a range of colours from red through pink or rose to several shades of yellow, to green and eventually to white simply by varying the amounts and ratios of the alloying metals, typically copper versus silver, zinc, nickel and palladium. This colour variation is well documented<sup>1-3</sup> and is illustrated in the well-known colour triangle, Figure 1, for gold-copper-silver alloys. Mark Grimwade has discussed this topic on several occasions at previous Santa Fe Symposia<sup>4</sup>.

More interestingly and not so well-known, it is also possible to produce carat gold jewellery in unusual colours such as purple, black, brown and blue. Gold jewellery with such colour effects is commercially available and becoming increasingly popular. Some of these exotic colours are obtained by alloying gold with certain other metals to produce special alloy structures known as intermetallic compounds. The other colours are obtained by forming oxides or patinas on the jewellery surface by chemical or thermal treatments, similar to those used to colour cast bronze sculptures, or by coating the surface with thin layers of other materials. Of course, it is possible to colour carat golds and the other precious metals by coating the surface selectively with glass enamels in a wide range of colours, but that is another, separate topic and will not be discussed in this paper.

In some parts of the industry, there is much mystery in how such colours are produced. It is not easy to find a ready source of information covering this topic. It is useful, therefore, to review the technologies involved in producing these special gold colours, as these have not, to my knowledge, been previously reviewed in a comprehensive manner. That said, Rapson<sup>3</sup> and, more recently, Cretu and van der Lingen<sup>6</sup> have reviewed some aspects. In addition, some of the possible techniques for producing black golds have been recently reviewed by Faccenda at the Santa Fe Symposium<sup>5</sup>.

In presenting this paper, the focus is naturally on gold but I will make reference to some special colours that can be obtained in the other precious metals and also highlight other potential approaches to broaden the range of colours for jewellery (and watch) applications that may emerge in the future.

### **The Coloured Intermetallic Compounds**

Many metals, including gold and platinum, when alloyed with certain other metals at a fixed composition, can form intermetallic compounds, some of which have intrinsic attractive colours. In simple terms, these are analogous to chemical compounds

where the different metal atoms combine in fixed ratios to form a particular compound. In the case of gold, we are familiar with the hardening caused in copper-rich carat golds of 18 and lower caratages, which results from the ordered intermetallic compounds, AuCu and AuCu<sub>3</sub>. Here the compounds are formed in the atom ratios of gold:copper of 1:1 and 1:3 respectively, i.e 50 atomic % gold : 50 at% copper and 25 at% gold : 75 at% copper.

In some binary alloy systems, the intermetallic compound occurs at a defined fixed composition and in others, it can occur over a narrow range of composition. The former often obey the chemical valency laws, whilst the latter are known as electron compounds. In general, intermetallic compounds are thermodynamically very stable and tend to be very hard and intrinsically brittle phases; they are not malleable and cannot be fabricated into complex shapes by conventional working techniques. Thus, their use in jewellery manufacture is not straightforward.

### ***The coloured gold intermetallics***

There are three gold intermetallic phases known to have attractive colours. Of these, the most well known is the gold-aluminium compound, AuAl<sub>2</sub>, which has an intense purple or violet colour, Figure 2a. It is known as 'purple gold' or sometimes as 'amethyst gold'.

The purple intermetallic phase, AuAl<sub>2</sub>, (more strictly described<sup>7</sup> as Au<sub>6</sub>Al<sub>11</sub>) occurs at 32.9 – 33.9 atomic % gold, which is about 79 weight % gold – 21 wt% aluminium<sup>8</sup>. Thus, it is theoretically hallmarkable as 18 carat gold. It can be formed in the bonds of gold wires and aluminium pads in electronic device manufacture if subjected to temperatures in excess of 250°C, causing joint embrittlement and failure. In the electronics industry, this phenomenon is known as the purple plague!

The other two coloured gold intermetallics are the gold-indium compound at 46 wt% gold, AuIn<sub>2</sub>, which has a clear blue colour<sup>6,9</sup> and melts at 544°C, and the gold-gallium compound at 58.5 wt% gold, AuGa<sub>2</sub>, which has a bluish hue<sup>6,9</sup>.

The reflectance curves for these 3 purple and blue intermetallics are shown in Figure 3, taken from reference 9. For AuAl<sub>2</sub>, like pure gold, there is a strong reflectance at the red-yellow end of the spectrum but, unlike pure gold, there is also a strong rise in reflectance at the blue-violet end of the spectrum, which results in the reddish purple colour. For the indium and gallium intermetallics, the drop in the middle of the spectrum is less marked, particularly for the gallium compound, and the red end of the spectrum is less strong, hence the blue colouration.

The Cielab colour co-ordinates for these compounds have also been measured<sup>6,10</sup> and are plotted on the graph in Figure 4 (The value of a\* differs between these two references, with Cretu & van der Lingen<sup>6</sup> giving a\* at just over 15 versus about 10 in the Figure).

Recently, Mark Grimwade<sup>41</sup> has told me of old German literature, dating back several decades (to 1937) in which it is reported that in the gold-potassium system, two intermetallics are coloured: Au<sub>4</sub>K (at 4.7% potassium) which is olive green and Au<sub>2</sub>K (at 9% potassium) which is violet (purple), but is sensitive to the air and 'needle-like'. Also the gold-rubidium intermetallic, Au<sub>2</sub>Rb is a deep green. These are unlikely to be practical for jewellery use.

### ***Use of gold intermetallics in jewellery***

Solid pieces of these gold intermetallics can be made by vacuum melting gold and aluminium in the correct ratio and casting. As mentioned earlier, these will be brittle and cannot be worked in the traditional manner. However, they can be applied to a substrate, such as a conventional carat gold, by thermal spraying in a gas jet. For purple gold, this involves use of molten gold-aluminium alloy powders, either alone or with gold and aluminium powder<sup>11</sup>. The molten alloy particles impact and stick to the substrate surface to give a purple gold decorative coating. Physical Vapour Deposition (PVD) techniques such as sputtering or evaporation of gold and aluminium can also be used to produce purple gold coatings. Jewellery with such purple gold coatings has been produced commercially.

Mintek in South Africa have shown the use in jewellery of purple gold that has been faceted into a pseudo-gem stone by machining<sup>6</sup>, Figure 2b. If the alloy is aluminium-rich (versus stoichiometric composition, then two phase alloys comprising dendrites of AuAl<sub>2</sub> and aluminium solid solution result. The purple colour is diluted towards that of aluminium. On the gold-rich side, the second phase that appears is another intermetallic, AuAl. According to reference 12, the purple colour is preserved down to 15% of aluminium. However, work by Leach & Garner<sup>10</sup> has shown that the purple colour is quickly lost as the composition deviates from stoichiometric, Figure 5.

Other techniques for making purple gold include powder metallurgy. A Japanese patent<sup>13</sup> claims additions of 7-30% of cobalt, nickel or palladium powders to gold-aluminium powders, which are pressed and sintered. These give a purple gold material with satisfactory workability, it is claimed. A similar patent was granted to Singapore Polytechnic in 2000<sup>14</sup> and purple gold jewellery made under this patent is marketed by Aspial Corporation. In a new Japanese patent<sup>15</sup>, ornamental purple gold alloys comprising 70-85% gold, rest aluminium are vacuum melted and atomised to powder. This is pressed in a mould and sintered by electric discharge heating.

Another approach is through bundling of aluminium-coated gold and gold-coated aluminium wires together and drawing them down to a composite wire. These are then subjected to a thermal diffusion treatment in a reducing atmosphere at 450-700°C. In this way, a fibrous wire of purple gold is produced, with some gold in a two-phase structure, that is tough and flexible<sup>16</sup>. Simply depositing an aluminium layer onto a gold surface and doing a diffusion treatment to produce a purple gold coating is also possible, it is claimed.

In another Japanese patent<sup>17</sup> by Seiko, gold articles with a purple colour comprise AuAl<sub>2</sub> particles embedded in a conventional high-gold matrix of gold-copper-silver alloy. This suggests that there is a measure of workability in such materials.

Some of these patents suggest that it is possible to obtain some measure of workability in purple gold intermetallic materials that contain second phases. In another patent<sup>18</sup>, the brittleness of AuAl<sub>2</sub> can be overcome by obtaining the material with a very fine grain size of below 50 microns, which can be achieved by hot working or quenching. In this patent, specific mention is made of the composition Au 34 at.% – Al 66 at.% and a ternary alloy, gold 31at.% - copper 3% - aluminium 66%. What the effect of some copper is on colour is not specified. Recent, unpublished work by Friso et al<sup>42</sup> on a 75 wt.% gold – aluminium- copper alloy, Figure 2c, indicates that increasing copper to 10 wt.% moves the colour to a pink, less intense hue and the difference in alloy microstructure is shown in figure 2d. The primary dendrites are AuAl<sub>2</sub>.

The use of the blue intermetallic compounds in commercial jewellery appears to be more limited. This is due to their very pale blue colour and relative softness (about HV 140), so tending to scratch easily<sup>38</sup>.

### ***Other coloured precious metal intermetallics***

Probably the best known of other precious metal intermetallic compounds is the platinum-aluminium compound, PtAl<sub>2</sub>, which is a golden yellow and contains 78% platinum. According to Cahn<sup>18</sup>, the addition of some copper moves the colour to an orange-pink. He reports that both forms have been used for jewellery and Mintek in South Africa have marketed PtAl<sub>2</sub> with copper additions as a pseudo-gem stone under the trade name 'Platigem'<sup>39</sup>, Figure 6. By varying the platinum, aluminium and copper ratios in the range 58-80% platinum, the colours range from dusty pink through a subtle orange to a rich yellow<sup>40</sup>. The gemstone buttons can be prepared by melting in inert atmospheres and then cabouched or faceted to shape, if desired. The faceted approach involves some polishing.

The PtGa<sub>2</sub> and PtIn<sub>2</sub> intermetallics are also yellow and PdIn is red unless there is an excess of palladium, when it is yellow<sup>18</sup>.

This is confirmed by Argarwal and Raykhtsaum<sup>10</sup>, who report that the palladium-indium compound, PdIn, has a reddish copper-yellow colour and that deviations from stoichiometric composition result in a rapid loss of colour, in a manner similar to that shown for AuAl<sub>2</sub>, Figure 5 (b). The addition of some silver to this compound causes a more yellow (less red) colour.

It is very possible that there are other coloured precious metal intermetallics, as yet, not reported in the literature. Whether any of these will have attractive strong colours of interest for jewellery is open to question.

### **Colours on precious metal surfaces: oxides, patinas and coatings**

We are all familiar with the turquoise blue patination of copper on roofs, the various brown-black patinas that grow on bronze sculptures and the tarnishing of silver and low carat golds, where the surface is slowly blackened by the formation of complex silver-copper sulphides due to corrosion by sulphur-containing species<sup>20</sup>. All these are examples of natural patinas, i.e. coloured surface layers arising from chemical reaction of the environment (corrosion) with one or more metals of the objects. The first two are examples of corrosion reactions deliberately exploited for decorative effect whereas the tarnishing of silver and gold is considered detrimental rather than decorative.

It is, of course possible to create coloured patinas artificially by immersion of the objects in various chemicals<sup>21, 22</sup> and cast bronzes are frequently subject to such treatments. It is also possible to artificially generate oxide (or anodised) layers on aluminium, titanium and niobium jewellery<sup>23</sup> that are naturally coloured, or coloured due to optical interference effects or can be coloured by incorporation of dyes into the anodised layer.

Such techniques are also used for colouring surfaces of gold and other precious metal jewellery:

#### ***Black – Grey Gold***

As Faccenda has already discussed<sup>5</sup>, there are several approaches to obtaining a black surface layer on carat gold jewellery:

- Electroplating

- Oxidation
- Chemical vapour deposition (CVD) of amorphous carbon

To this list we should also add:

- Patination

Electroplating: Typically, a range of black surface effects can be achieved on carat gold and other precious metal jewellery by electroplating with so-called 'black rhodium' or 'black ruthenium'. These are special baths formulated with black additives to produce a hard black rhodium or ruthenium electroplated layer of up to 0.5 microns thickness on the surface. A post-plating treatment is necessary to give colour stability and wear resistance. The colours range from grey to anthracite black. Hardness values typically range from HV230 - HV310, the hardness depending inversely on the amount of black in the coating. Wear resistance is claimed to be good. Details of the plating process are given in reference 5.

It is possible to electroplate black gold coatings but these are not stable over time<sup>24</sup>, although black and grey gold electroplating systems based on gold-nickel baths are commercially available<sup>37</sup>.

Oxidation: Whilst annealing of conventional carat golds in air will produce a black copper oxide layer, this is not physically stable or durable. Consequently, special gold alloys have been developed to produce good, stable black oxide layers. Many of these contain cobalt, which forms a dense black oxide when the gold alloy is subjected to an oxidation treatment. This is done on the finished article; the black oxide can be subsequently polished by buffing to produce a quality finish. Alloys of gold with nickel or iron additions are also claimed to give grey-black oxides.

A patent by Tanaka KKK in Japan<sup>25</sup> claims cobalt-containing alloys that form lustrous black cobalt oxide layers 0.1-10 microns thick. This patent is also applicable to platinum and silver alloys. In US patent 5,139,739, Takayanagi et al<sup>26</sup> claim gold alloys that contain at least one metal from the group copper, iron, cobalt and titanium, and also possibly one from the group comprising the 6 platinum group metals, silver and nickel. In their examples, cobalt and iron are the major additions to a range of 10, 14 & 18 ct golds, each typically in the range of 5-20%. Oxidation is carried out in air at 700-950°C for times of about 20-60 minutes. Some commercial Japanese jewellery made under this patent is shown in Figure 7 and other examples of commercial jewellery made by oxidation are shown in Figure 8.

Improved wear resistance of black gold can be obtained in 18 carat golds made from cobalt-containing alloys through chromium additions<sup>27</sup> and the use of an electrolytic hardening cycle. The addition of chromium results in thinner oxide layers, comprising mostly chromium oxide, Cr<sub>2</sub>O<sub>3</sub>, which have an olive-green hue. The oxide on an 18ct 15% cobalt- 10% chromium alloy had better wear resistance than that on an 18 ct-25% cobalt alloy<sup>6</sup>.

Amorphous carbon by CVD: The deposition of hydrogenated amorphous carbon layers on gold by plasma assisted chemical vapour deposition for watch applications has been discussed by Faccenda<sup>5</sup>. This process operates at 200-400°C (390 – 450°F) and produces a hard black coating, 1.0 – 1.5 microns thick, with good resistance to wear and impact and with an appearance of Chinese Lacquer. The hardness of this layer is very high, about HV 1800 – HV2000. It can also be applied to other jewellery metals as well as gold. Wear tests showed this coating to be superior to electrodeposited black ruthenium.

***Patination:*** The application of chemical treatments containing oxygen and sulphur compounds can result in black and other colours on carat golds, generally through reaction with the copper in the alloy<sup>21</sup>. The oldest technique consists of immersing the items in impure potassium sulphide salts, known as 'Liver of Sulphur'. Other liquid sulphides and polysulphides are also used, preferably in diluted form to allow the films to build up more slowly but denser and more permanent. Untracht<sup>21</sup> suggests immersing the carat gold hot to produce a black colour or to use additions of 'aqua ammonia' (ammonium hydroxide) in the solution at room temperature. Immersion in barium sulphide solutions will produce a bluish-black coloration.

### ***Brown Gold***

Chocolate brown gold jewellery is currently being marketed as the latest fashion trend, Figure 9. Like black gold, this colouration is formed by a surface layer. The method used is not disclosed but is probably an oxidation technique. Physical Vapour Deposition (PVD) of brown zirconium nitride is also used<sup>35</sup>. Patination by immersion in Liver of Sulphur is another method discussed by Untracht<sup>21</sup>.

Oxidation of gold alloys is achieved on special gold alloys. Brown oxides can be obtained with metals such as iron, manganese, nickel and copper, so that incorporating these metals into carat golds and oxidising them under controlled conditions produces brown oxides on the surface. Bright brown colours, based on this approach, are claimed in a Japanese patent<sup>33</sup> by Takayanagi of AIST for gold – silver (< 30% Ag) or gold-nickel-manganese (<30% Ni & 5-40% Mn) alloys containing 60-95% gold. The thickness of the brown layer and the degree of brownness increases with time of oxidation.

### ***Blue Gold***

Blue layers can be obtained by oxidation of carat golds containing special additions. Jewellery with such colour was launched in 1988 by VA Blue Gold SA of Switzerland<sup>28</sup>, based on the patent by Muller<sup>29</sup>, Figure 10. In this, 18 – 23 carat golds containing iron and a little nickel are oxidised at 450 – 600°C (840 – 1110°F) for 10-12 minutes. For an 18 carat alloy containing 24.4% iron and 0.6% nickel, a blue-green colour is obtained whereas for a 20 carat gold containing 14.4% iron and 0.6% nickel, a good blue colour is developed.

Kretchmer<sup>29</sup> has also developed blue gold jewellery that obtains its blue coloration from an optical interference effect on the oxide film, Figure 11. Gold alloys with 25% arsenic or iron are also known to produce blue colours. Friso et al<sup>42</sup> have shown recently that a 75% gold -23% iron-2% copper alloy forms a blue colour on oxidation at 400 – 500°C, Figure 12. When 2% chromium is added to this alloy, as well as a blue colour, an intense reddish-violet colour is obtained at low oxidation temperatures.

Currently, the jewellery company, Jarretiere, of Italy is marketing jewellery collections with blue gold, Figure 13, both bluish black and true blue colours, as well as black gold, all by oxidation techniques.

### ***Future New Colours***

It has been said that totally new special (unusual) colours for gold are unlikely to emerge. However, there is some evidence that suggests this statement may not be entirely true. I present some observations and conjecture below. It is, of course, arguable whether such colours are desirable! There are some who believe that terms such as 'black gold' and 'blue gold' are misnomers and should not be used as the gold alloy itself is not intrinsically of these colours<sup>30</sup>.

### **Green Gold**

A new patent<sup>34</sup> by Takayanagi of AIST, Japan concerns production of a green gold by a patination technique on copper-containing carat golds in the range 15-67.5% copper. This produces what is described as a thin 'verdigris' film on the surface. A number of chemical mixtures are described to produce the green patina, many involving copper salts. I am not aware that green gold jewellery produced by patination is yet commercially available, although conventional green carat gold jewellery in gold-silver is commercially produced.

### **Red Gold**

As stated in the section on blue gold, Friso et al<sup>42</sup> have shown it is possible to get an intense reddish-violet colour on low temperature oxidation of a 18 carat gold-iron-copper- 2% chromium alloy, Figure 14.

### **Coloured rhodium electroplating systems**

Recently, blue and red rhodium electroplating systems have been developed<sup>36,37</sup>, analogous to black rhodium, although their application to carat gold jewellery has not yet materialized. Presumably, the blue and red colours are obtained with coloured additives to the bath, like the black version. Abrasion-resistant coatings of black, blue or red rhodium, up to 0.3 microns thick and with a gloss, can be plated in 30-90 seconds, it is claimed<sup>36</sup>. They can be put on gold, silver and nickel.

### **Colours through Boronising Treatments**

In their paper presented at the 1984 IPMI conference, Matsuda and co-workers<sup>31</sup> studied the surface hardening of gold alloys by boronising treatments. The gold alloy is immersed in boron powder and subjected to thermal treatments at 900-950°C (1650- 1740°F) for about 6 hours. It was found that pure gold does not respond to boronising treatments but the alloying metals in gold alloys do react. Interestingly, in additional experiments, some binary alloys of gold with up to 15% of alloying addition were rolled to sheet and boronised at 850°C for up to 48 hours. This showed that some alloys produced layers with marked colours, as shown in Table 1.

TABLE 1: Colours produced on boronised gold alloys (up to 15% alloying addition)<sup>29</sup>

<b>Alloy</b>	<b>Colour</b>
Gold – lanthanum Gold - cerium Gold – neodymium	Purple blue or blue
Gold – holmium	Deep grey
Gold – beryllium	Red – purple
Gold – manganese	Yellowish – brown
Gold – yttrium	No change

This is an interesting observation that suggests an alternative approach to surface colouration of gold alloys. As far as the author knows, this work has not been followed up. As well as sulphides and borides, possibly other compounds such as nitrides, selenides and silicides could be fruitful avenues of exploration? After all, titanium nitride is gold-coloured!

### ***New intermetallic colours***

As noted earlier, the three coloured intermetallic compounds of gold are binary alloys. Argarwal and Raykhtsaum<sup>10</sup> noted that silver additions to AuAl<sub>2</sub> shifted the colour towards yellow and presumably other additions may have a different effect for all 3 intermetallic compounds. In the case of platinum, Cahn<sup>19</sup> noted that additions of copper to PtAl<sub>2</sub> shifted the yellow colour to an orange-pink. Again, these observations do not appear to have been pursued further, with the exception of the Platigem range of 'gemstones' developed by Mintek. They do suggest that ternary or higher intermetallic alloys could yield new colours, analogous to shifting band-gap colour pigments such as the cadmium sulphides, used in plastics and ceramic enamels.

### ***Colloidal gold colours***

Ruby red glass is coloured by colloidal suspensions of gold nanoparticles. The same effect is used for purple-red to pink decorative glass enamel for tableware and glass. Colloidal gold, known as 'Purple of Cassius', is an ancient technology<sup>32</sup>. Colloidal silver is yellow and alloys of colloidal gold and silver are used in decorative glass enamels to shift the purple colour towards pink.

In the current exciting world of nanotechnology research, nanoshells are an interesting development. They consist of a metal such as gold coated onto a dielectric core such as silica. These absorb light and so have a characteristic colour that depends on the relative metal thickness:core size. The colour is produced by a plasmon resonance mechanism. When the gold shells are made thinner, the purple colour shifts to greens and blues. Maybe, this effect could be used to create some novel glass enamels for jewellery use? Use of platinum and other precious metal nanoshells could also yield some interesting colour effects.

### **Conclusions**

I have attempted to demonstrate that gold jewellery can be made with some special (unusual) colour effects, either due to intrinsically coloured intermetallic phases or to surface layers grown by reaction with alloying metals or by deposition techniques. A wide range of colours such as blue, black, brown and purple can be achieved and a number of techniques employed. However, there are some drawbacks: intermetallic colours are intrinsically brittle and surface coatings by any technique are liable to be fragile and will spall if knocked and wear away if rubbed constantly.

I have also indicated that other precious metal jewellery such as platinum and silver can also be coloured by the same techniques, although the total range may not be as impressive as with gold.

Lastly, I have speculated on the scope for new colour effects and the possible technical approaches to develop them.

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## References

1. Rose, T.K. and Newman, W.A.C., "The Metallurgy of Gold", 7<sup>th</sup> Ed., *Charles Griffin & Co.*, 1937, Reprinted by *Met-Chem Research Inc.*, 1986, p56-59
2. Gmelin's Handbuch der Anorganischen Chemie., 8<sup>th</sup> edition, System No 62, "Gold", 1954, p954-956.
3. Rapson, W.S., and Groenewald, T., "Gold Usage", *Academic Press*, 1978, p30-85.
4. Grimwade, M.F., "The Nature of Metals and Alloys", Proc. Santa Fe Symposium, 2001, *Met-Chem Research Inc.* p151-180
5. Faccenda, V., "Advanced Technology for the Jewelry Industry", Proc. Santa Fe Symposium, 2002, *Met-Chem Research Inc.* p177-188
6. Cretu, C. and van der Lingen, E., *Gold Bulletin*, **32 (4)**, 1999, p115-126 and *Gold Technology*, no 30, 2000, pp31-40
7. Rapson, W.S., "Intermetallic Compounds of Gold", *Gold Bulletin*, **29 (4)**, 1996, p141-142
8. "Phase Diagrams of Binary Gold alloys", ed. Okamoto, H. & Massalski, T.B., *ASM International*, 1987, p13
9. Saeger, K.E. and Rodies, J., "The Colour of Gold", *Gold Bulletin*, **10(1)**, 1977, p10-14
10. Agarwal, D.P. and Raykhtsaum, G., "Color Technology for Jewelry Applications", Proc. Santa Fe Symposium, 1988, *Met-Chem Research Inc.* p229-244
11. Derouwaux, P. and Hofman, C., Swiss patent 533,691, 1973
12. Hori, S. *et al*, "The Use of Precious Metals in Jewelry and Ornaments", in "*Precious Metals Science and Technology*", *IPMI*, 1991, p421-470
13. Fukayama, S., Japanese patent JP62240729, 1987 (Seiko Instruments)
14. Loh, P.C., World patent WO 00/46413, 2000 (Singapore Polytechnic)
15. Yamazaki, S, Ishii, N. and Sawada, K., Japanese patent 2003183710, 2003 (Ishifuku Metal Industry)
16. Yukio, M., Japanese patent JP4176829, 1992 (the Pilot Corp)
17. Japanese patent JP2115329, 1991 (Seiko Epson Corp)
18. Steinemann, S., European patent EP 284699, 1988
19. Cahn, R.W., "A Precious Stone that Isn't", *Nature*, **396** 10 December 1998, p523-524
20. Corti, C.W., "High Carat Golds do not Tarnish", Proc. Santa Fe Symposium, 2000, *Met-Chem Research Inc.* p29-56
21. Untracht, O., "Jewelry Concepts and Technology", *Robert Hale Ltd*, 1982, chapter 17, p714-730
22. Hughes, R. and Rowe, M., "The Colouring, Bronzing and Patination of Metals", *pub by?*, date?
23. For example, Seeley, B., "Niobium: A Primer in the Semi-Precious", Proc. Santa Fe Symposium, 2003, *Met-Chem Research Inc.* p357-372
24. Personal communication, F.Simon, Umicore Galvanotechnik, 2003
25. Nakama, K, European patent EP 0438 980, 1991 (Tanaka KKK, Japan)
26. Takayanagi, T. *et al*, US patent USP5,139,739, 1992 (AIST & Seki Co, Japan)
27. Van Graan, L. and van der Lingen, E., *MSSA Proc.*, ed. M.McClean *et al*, *Microscopy Soc. of S.Africa*, **28**, 1998, p19
28. Muller, L., US patent USP 5,059,255, 1991 (Ludwig Muller SA, Switzerland)
29. Lutwak, M. and York, Y., "Kretchmer's Blues", *Aurum*, No 34, 1989, p36-38

30. Gainsbury, P., "Colour in Gold alloys", *Aurum*, no 20, 1984, p40-41
31. Matsuda, F., Nakata, K., Tohmoto, K. and Morikawa, M., "Surface Hardening of Gold with Boronizing Technique", in "*Precious Metals*", ed. Mohide, T.P., *IPMI*, 1984, p131-145
32. Hunt, L.B., "The True Story of Purple of Cassius", *Gold Bulletin*, **9(4)**, 1976, p134-139
33. Takayanagi, T., *et al*, Japanese patent JP 2185934, 1990 (AIST)
34. Takayanagi, T. Japanese patent JP 2002191421, 2002, (AIST)
35. V.Facenda, Private communication, 2004.
36. Leaflet from Oftec GmbH, Germany 2004 (black, blue and red rhodium)
37. Leaflet from Pino Aliprandini SA, Switzerland, 2004 (black & blue rhodium)
38. Private communication, E. van der Lingen, Mintek, May 2004
39. US patent 5,045,280; South African patent 90/7777
40. Hurlly, J. and Wedepohl, P.T., "Optical properties of coloured platinum intermetallic compounds", *J.Mats. Sci.*, **28**, 1993, 5648-5653
41. Private communication, M.F. Grimwade, May 2004. [See 'Phase Diagrams of Binary Gold Alloys', ed. H.Okamoto & T.B.Massalski, ASM International, 1987, p155 for references on Au-K colours]
42. Unpublished work, Friso, A., Magrini, M., Dabala, M., Poliero, M., & Basso, A., University of Padua, Italy, 2004

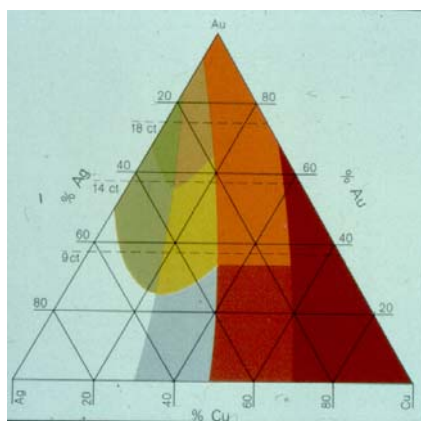


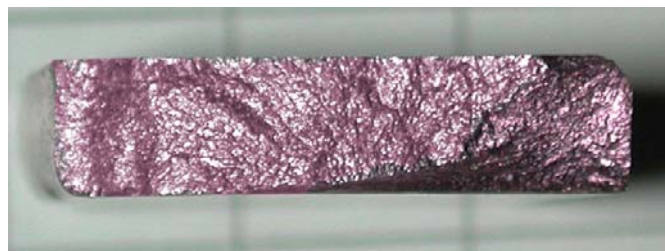
Figure 1 The Colour of Gold-Copper-Silver Alloys



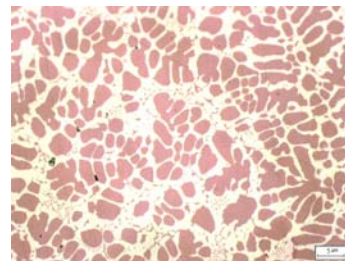
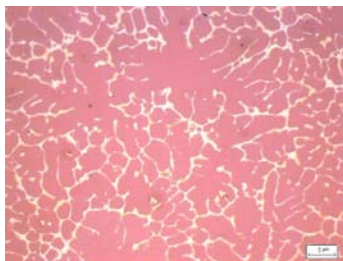
Figure 2 (a) Purple gold pendant (taken from reference 30)



(b) Purple gold machined into a pseudo-gem stone (Courtesy Mintek)



(c) Purple gold, 75%gold -20%aluminium – 5% copper ingot (broke on rolling) Courtesy Friso et al (42)



(d) Microstructure of 75% Au- Al alloys with 5% copper (left) and 10% copper (right). Courtesy Friso et al (42) X 500

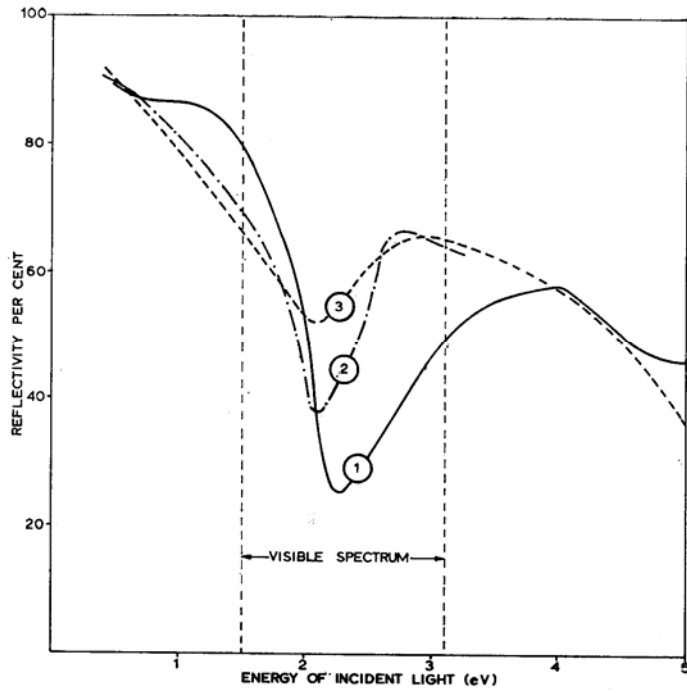


Figure 3 Reflectivity curves for 3 gold intermetallic compounds (from Saeger & Rodies<sup>9</sup>): Curve 1 – AuAl<sub>2</sub>, Curve 2 – AuIn<sub>2</sub>, Curve 3 – AuGa<sub>2</sub>

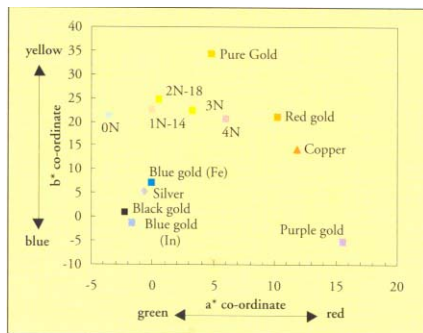
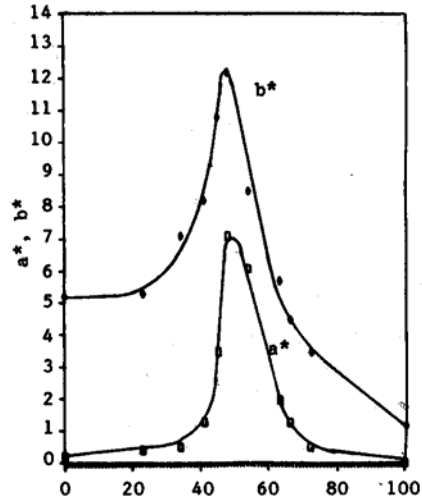
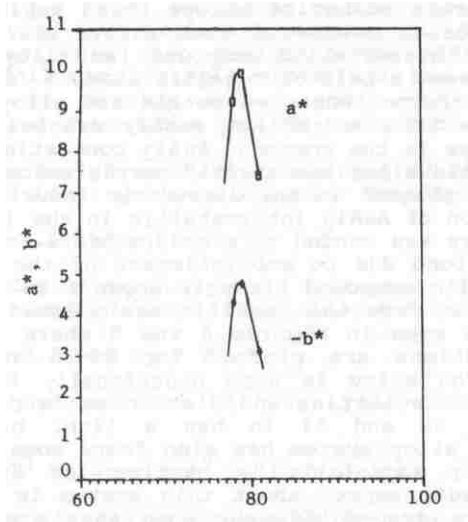


Figure 4 CIELab co-ordinates of coloured gold alloys (from Cretu & van der Lingen<sup>6</sup>)



(a)

(b)

Figure 5 Effect of deviation from Stoichiometric composition on CIELab coordinates for (a)  $\text{AuAl}_2$  and (b)  $\text{PdIn}$  intermetallics (from Agarwal and Raykhtsaum<sup>10</sup>)



Figure 6 Platigem jewellery, courtesy Mintek



Figure 7 Black gold jewellery, courtesy Seki Co and Mitsubishi Materials Corp, Japan



Figure 8 Black gold jewellery by Jarretiere, Italy (left) and Yvel, Israel (right)



Figure 9 Brown gold jewellery by Yvel, Israel



Figure 10 Blue gold jewellery: Left - 22ct gold by Vittorio Antoniazzi, Right - 'Heart' collection, Ludwig Muller



Figure 11 Blue gold jewellery by S.Kretchmer (29)

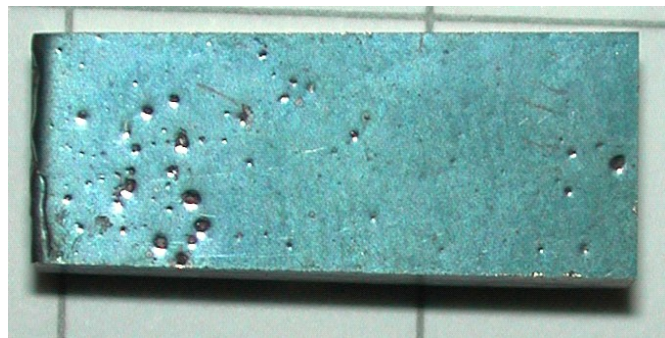


Figure 12 75% Au -23%Fe -2%Cu oxidised at 400 – 500°C, Friso et al (42)



Figure 13 Blue gold jewellery by Jarretiere, Italy

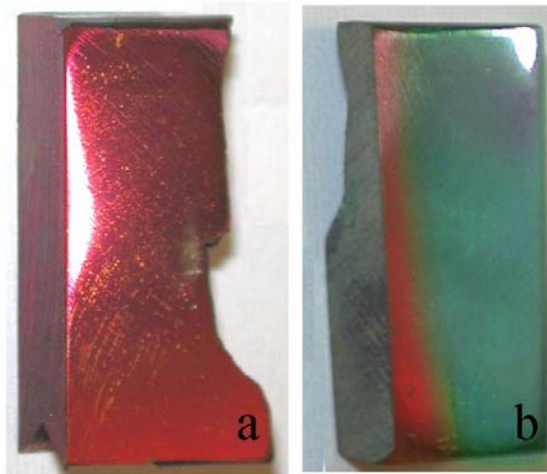


Figure 14 (a) Red colour on 18 carat Au-Fe-Cu +2%Cr at low oxidation temperatures [higher temperature gives blue colour, (b)]. Friso et al (42)